

Current efficiency and crystallization mechanism in pulse plating of hard chromium

P. LEISNER, G. BECH-NIELSEN, P. MØLLER

Centre of Advanced Electroplating, DTH 425, DK-2800 Lyngby, Denmark

Received 9 December 1991; revised 14 May 1993

The current efficiency of chromium deposition was investigated under conditions of periodic current reversal. It has been demonstrated that the relationship between the anodic and the cathodic charges, Q_a/Q_c , has a strong influence on the current efficiency and the structure of the deposit. A plausible model for the crystallization mechanism during periodic current reversal has been suggested. According to the model, an advantageous chromium structure is maintained during the deposition process because interstitial hydrogen in the chromium lattice is oxidized during the anodic period.

Notation

F	Faraday constant
i_a	anodic current density
i_c	cathodic current density
m_a	mass of dissolved chromium
m_c	mass of deposited chromium
M	molecular weight of chromium
Q_a	anodic charge
Q_c	cathodic charge
T	cycle time ($T_c + T_a$)

T_a	anodic pulse duration
T_c	cathodic pulse duration

Greek symbols

θ	current efficiency
θ_a	current efficiency of chromium dissolution in anodic period
θ_c	current efficiency of chromium deposition in cathodic period
θ_{\max}	maximum current efficiency

1. Introduction

Electrolytic deposition of hard chromium is characterized by a low current efficiency (c.e.). In a traditional sulphate catalysed chromium bath the c.e. is typically 12–20%, while in modern special catalytic based baths it can exceed 30%. In general c.e. increases with current density (c.d.) and decreases with temperature. However, it has been observed that the c.e. in the sulphate catalysed chromium bath can be increased considerably by the use of low frequency periodic current reversal (p.r.) of short duration during the deposition process [1]. The effect of p.r. on the c.e. in modern baths has only recently been investigated [2].

The dependence of the c.e. on the pulse parameters has recently been investigated by Leisner *et al.* [1] who found that the most important parameter for the c.e. is the ratio between the electrical charges in the anodic and in the cathodic pulse, Q_a/Q_c (Fig. 1), where

$$\frac{Q_a}{Q_c} = \frac{i_a T_a}{i_c T_c} \quad (1)$$

It has been demonstrated that the c.e. has a maximum at a Q_a/Q_c value of approximately 0.007. Below this ratio the c.e. falls to that obtained under d.c. conditions, while the c.e. falls to even lower values when $Q_a/Q_c \gg (Q_a/Q_c)_{\text{optimal}}$. There are broad boundaries for the variation of the pulse parameters, with-

out influencing the c.e., as long as Q_a/Q_c remains constant. Leisner *et al.* performed the following variations without affecting the c.e.:

$$\begin{aligned} \text{Anodic c.d.: } i_a &= 4\text{--}1000 \text{ A dm}^{-2} \\ \text{Anodic pulse duration: } T_a &= 40\text{--}300 \text{ ms} \\ \text{Cycle time: } T &= 5\text{--}30 \text{ s} \end{aligned}$$

It was observed that, just as with d.c. plating, the c.e. increases with cathodic c.d. and decreases with temperature.

In the present work a thorough investigation has been performed of c.e. as a function of Q_a/Q_c at varying temperatures and cathodic c.d. On the basis of the results it is possible to present a model for the crystallization mechanism under conditions of p.r. plating of hard chromium.

2. Experimental details

Deposition took place at the base of steel cylinders (0.2 cm^2) following mechanical polishing and pickling in hydrochloric acid–ethanol–water with a volume ratio 2 : 2 : 1. Chromium was deposited from a sulphate catalysed chromium bath (CrO_3 250 g dm^{-3} , H_2SO_4 2.5 g dm^{-3}) during stirring. In each experiment a charge of approximately 90 C was passed. The c.e. was determined by measuring the layer thickness using an X-ray technique (Fischerscope X-ray 1550).

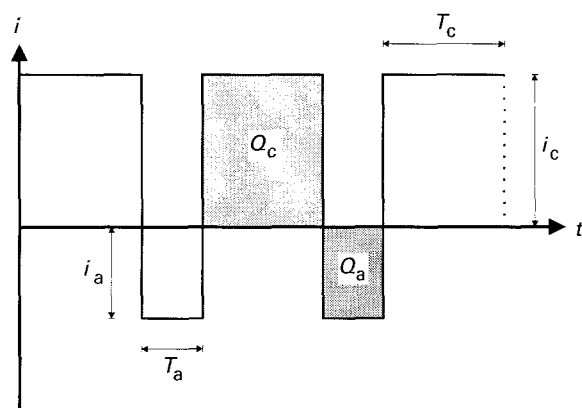


Fig. 1. Periodic current reversal.

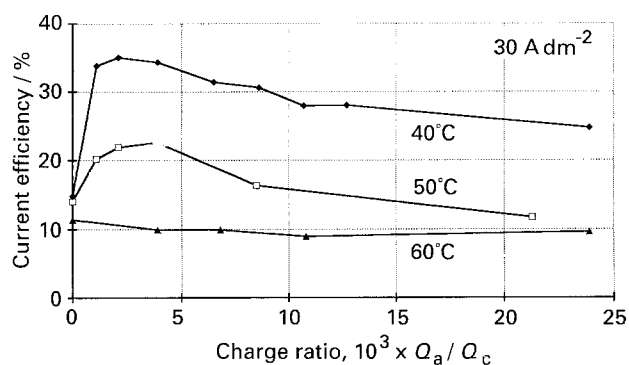
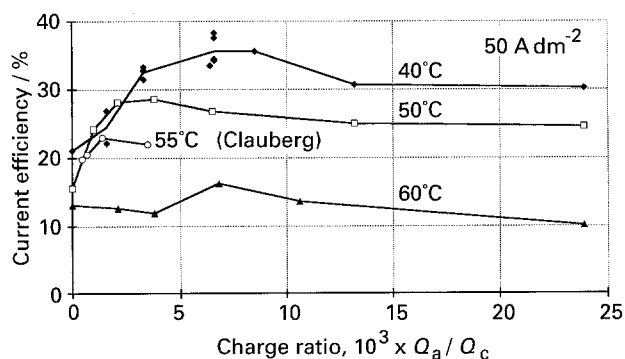
Table 1. Experimental results

Experiment	Temperature/°C	$i_c/A\text{ dm}^{-2}$	$i_a/A\text{ dm}^{-2}$	T_a/ms	T/s	$Q_a/Q_c \times 1000$	CE/%
1	40	30	0	0	—	0.0	14.8
2	40	30	16	30	15	1.1	33.8
3	40	30	16	60	15	2.1	35.0
4	40	30	16	110	15	3.9	34.3
5	40	30	24	120	15	6.5	31.4
6	40	30	16	240	15	8.6	30.6
7	40	30	160	10	5	10.7	27.9
8	40	30	16	350	15	12.7	28.0
9	40	30	30	350	15	23.9	24.7
10	40	50	0	0	—	0.0	21.1
11a	40	50	40	10	5	1.6	26.9
11b	40	50	40	10	5	1.6	22.2
12a	40	50	40	20	5	3.3	33.3
12b	40	50	40	20	5	3.3	32.8
13	40	50	20	40	5	3.3	31.5
14	40	50	32	300	30	6.4	33.5
15a	40	50	40	40	5	6.6	38.3
15b	40	50	40	40	5	6.6	37.6
16	40	50	80	20	5	6.6	34.5
17	40	50	20	80	5	6.6	34.3
18	40	50	26	240	15	8.5	35.6
19	40	50	40	80	5	13.2	30.7
20	40	50	50	350	15	23.9	30.2
21	50	30	0	0	—	0.0	14.0
22	50	30	16	30	15	1.1	20.2
23	50	30	16	60	15	2.1	21.9
24	50	30	16	110	15	3.9	22.6
25	50	30	4	300	5	8.5	16.3
26	50	30	80	40	5	21.3	11.7
27	50	50	0	0	—	0.0	15.5
28	50	50	26	30	15	1.0	24.2
29	50	50	26	60	15	2.1	28.1
30	50	50	26	110	15	3.8	28.6
31	50	50	82	60	15	6.5	26.8
32	50	50	160	20	5	13.2	25.0
33	50	50	50	350	15	23.9	24.6
34	60	30	0	0	—	0.0	11.4
35	60	30	16	110	15	3.9	9.9
36	60	30	100	60	30	6.8	9.9
37	60	30	16	300	15	10.8	8.9
38	60	30	30	350	15	23.9	9.6
39	60	50	0	0	—	0.0	13.1
40	60	50	26	60	15	2.1	12.6
41	60	50	26	110	15	3.8	11.9
42	60	50	14	120	5	6.8	16.2
43	60	50	26	300	15	10.6	13.6
44	60	50	50	350	15	23.9	10.1

3. Results

Results are collected in Table 1. C.e. as a function of Q_a/Q_c at various temperatures and cathodic c.d. is shown in Figs 2 and 3. The c.e. is calculated entirely on the basis of the amount of cathodic charge, Q_c . In Fig. 3 results of Clauberg [2] are also included. In these figures the d.c. results are shown at $Q_a/Q_c = 0$. Experiments 11, 12 and 15 were repeated twice in order to check the reproducibility of the results.

At temperatures below 60°C the maximum c.e. was found at Q_a/Q_c values between 0.0020 and 0.0085, while at 60°C there was no clear maximum.

Fig. 2. Current efficiency against Q_a/Q_c .Fig. 3. Current efficiency against Q_a/Q_c .

With regard to c.e. the optimal Q_a/Q_c value depended on temperature and cathodic c.d. in such a way that the optimal Q_a/Q_c value increased with falling temperature for cathodic c.d. of 50 A dm^{-2} , while the temperature dependence was modest at 30 A dm^{-2} .

The number of cracks in the chromium coatings decreased markedly with increasing Q_a/Q_c . Coatings deposited with optimal or higher Q_a/Q_c values were without cracks (Fig. 4).

4. Discussion

Before describing crystallization under p.r. conditions, it is relevant to describe crystallization under d.c. conditions [3–5]. D.c. deposition of hard chromium is accompanied by a considerable codeposition of hydrogen. A small part of the hydrogen is incorporated in the coating resulting in hexagonal chromium hydride (β -chromium), which is a metastable chromium structure, stabilized by hydrogen. β -chromium has a tendency to decompose into hydrogen gas and cubic space-centred chromium (α -chromium) containing a residue of dissolved hydrogen. Decomposition results in tensile stress, which leads to the formation of cracks in the coating. Under conditions of higher Cr(III) concentrations and lower temperatures than normal operating conditions it is possible to deposit relatively durable coatings consisting of β -chromium or a combination of α - and β -chromium. On the other hand deposition

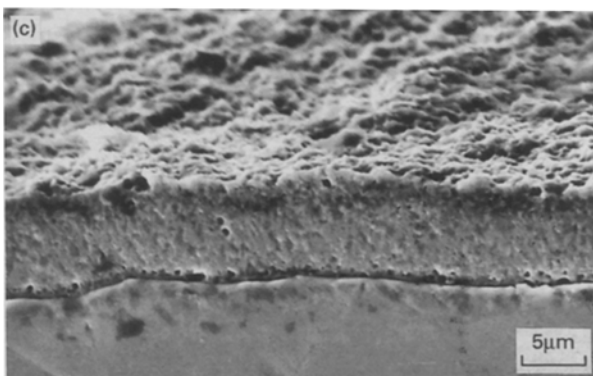
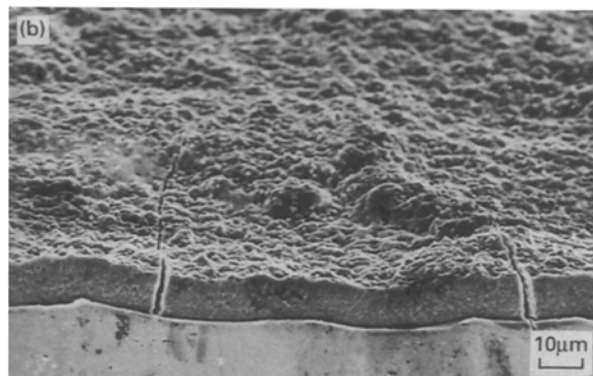
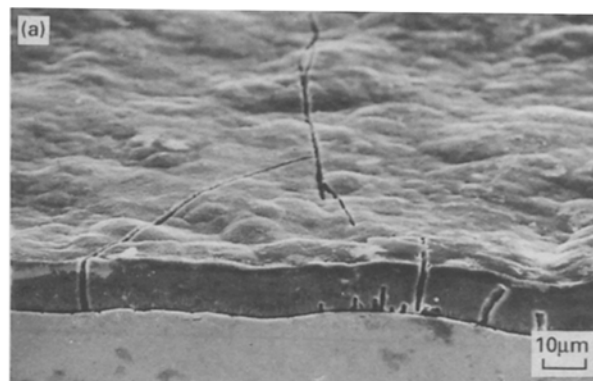


Fig. 4. Scanning electron micrographs of etched coatings produced at $i_{DC} = i_c = i_a = 30 \text{ A dm}^{-2}$, 50°C . (a) d.c., $Q_a/Q_c = 0.0000$; (b) $T_c = 15 \text{ s}$, $T_a = 10 \text{ ms}$, $Q_a/Q_c = 0.0007$; (c) $T_c = 15 \text{ s}$, $T_a = 60 \text{ ms}$, $Q_a/Q_c = 0.0040$.

of so-called crack-free chromium at temperatures above approximately 70°C and low c.d. produces a crack-free coating of α -chromium. This is apparently caused by direct deposition of α -chromium, or such a rapid decomposition of chromium hydride, that no inner tensions are produced, to the extent of producing cracks. In accordance with this conclusion Eilender *et al.* [6] have determined the hydrogen content in the chromium deposited at different temperatures and c.d. and found that the hydrogen content decreases with increasing temperature and to a lesser degree with decreasing c.d.

Christov and Pangarov [7] have investigated hydrogen evolution on α - and β -chromium, respectively, in weakly acid and weakly basic solutions. They found that both mechanisms and hydrogen overvoltage are different for the two modifications of chromium. Hydrogen overvoltage is greater for α -chromium

than for β -chromium. The difference in hydrogen overvoltage is 0.146 V at pH 2.7 and 0.227 V at pH 11.48.

On the basis of knowledge of d.c. deposition of chromium and the results obtained in the present work it is possible to suggest a plausible model for the crystallization mechanism under p.r. conditions.

Under p.r. conditions the structurally incorporated hydrogen is oxidized during the anodic period. By applying a sufficiently large value of Q_a/Q_c the hydrogen content in the coating is minimized, so that β -chromium is not formed. Therefore, during the cathodic period chromium deposits as α -chromium. This means that the phase alteration β -chromium \rightarrow α -chromium and the resulting production of cracks is avoided. Furthermore the high hydrogen overvoltage is maintained and the observed increase in c.e. is obtained.

If the anodic amount of charge is insufficient, the desired effect is only partially achieved, and the c.e. is at a level between d.c. plating and optimal p.r. plating, and at the same time cracks will develop in the coating.

The fact that c.e. also decreases at Q_a/Q_c values above the optimal value is explained by anodic redissolution of chromium as Cr(II), which is oxidized further to Cr(III) in solution. This dissolution reaction is described by the following. The c.e., θ_c , for the reduction of Cr(VI) to Cr(O) in the cathodic period is given by

$$\theta_c = \frac{m_c 6F}{Q_c M} \quad (2)$$

$$\Leftrightarrow m_c = Q_c \theta_c \frac{M}{6F} \quad (3)$$

Correspondingly the c.e. θ_a , for the oxidation of Cr(O) to Cr(II) in the anodic period is given by the following equation:

$$\theta_a = \frac{m_a 2F}{Q_a M} \quad (4)$$

When it is assumed that chromium oxidation proceeds with a c.e. of 100% after completion of hydrogen oxidation in the anodic period, the following equation can be added

$$\theta_a = 1 \quad \text{for} \quad \frac{Q_a}{Q_c} \geq \left(\frac{Q_a}{Q_c}\right)_{\text{optimal}} \quad (5)$$

The mass of dissolved chromium for $Q_a/Q_c \geq (Q_a/Q_c)_{\text{optimal}}$ is thus given by

$$m_a = \left[\frac{Q_a}{Q_c} - \left(\frac{Q_a}{Q_c}\right)_{\text{optimal}} \right] Q_c \frac{M}{2F} \quad (6)$$

The total c.e. (the metal efficiency), θ , for $Q_a/Q_c \geq (Q_a/Q_c)_{\text{optimal}}$ calculated on the basis of the cathodic amount of charge is thus given by

$$\theta = \frac{m_c - m_a}{Q_c} \frac{6F}{M} \quad (7)$$

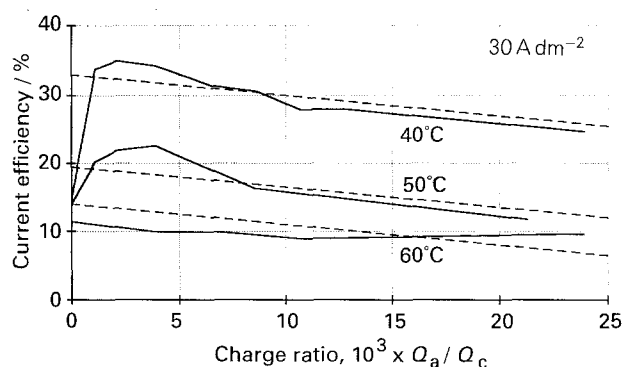


Fig. 5. Current efficiency against Q_a/Q_c . The slope of the dotted lines is -3.

Inserting Equations 3 and 6 in Equation 7, one obtains

$$\theta = \theta_{\text{max}} - 3 \left[\frac{Q_a}{Q_c} - \left(\frac{Q_a}{Q_c}\right)_{\text{optimal}} \right] \quad (8)$$

A plot of θ against Q_a/Q_c will thus be linear with a slope of -3 for $Q_a/Q_c \geq (Q_a/Q_c)_{\text{optimal}}$. Since the results of the present work conform to this model (Figs 5 and 6) it is highly probable that an anodic charge exceeding the optimum with respect to c.e., will cause oxidation of Cr(O) to Cr(II) at a c.e. of 100% with the c.d. used here.

The preceding considerations are in agreement with work by Kakoykina and Sysoev [8] who were unable to deposit chromium at $Q_a/Q_c = 0.100$, but obtained chromium deposits in low yield with Q_a/Q_c values between 0.025 and 0.033.

5. Conclusion

The dependence of c.e. on bath temperature, cathodic c.d. and Q_a/Q_c have been investigated under p.r. conditions. A report by Colombini [9] stating that the c.e. increases with decreasing cathodic pulse time and increasing anodic c.d. (that is to say, increasing Q_a/Q_c), is only correct within a narrow boundary of Q_a/Q_c values, since a continued reduction of the cathodic pulse time, or an increase of the anodic c.d., will lead to falling c.e. because of the redissolution of chromium. The optimal c.e. is obtained with

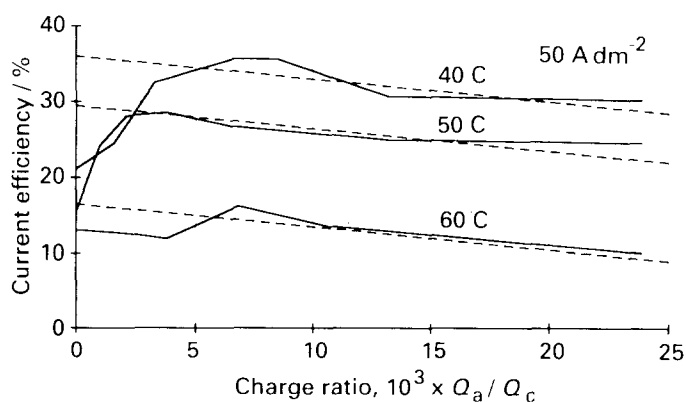


Fig. 6. Current efficiency against Q_a/Q_c . The slope of the dotted lines is -3.

Q_a/Q_c values between 0.0020 and 0.0085. Increase of the c.e. is greatest at relatively low temperatures.

On the basis of the present work and other literature a crystallization mechanism for the deposition of chromium under p.r. conditions has been proposed.

With industrial production one should be aware of the fact that the use of relatively high Q_a/Q_c values will result in increased production of Cr(III) in the bath. In order to avoid this, Q_a/Q_c should be carefully chosen on the basis of the other process parameters. In addition, it is desirable to increase the anode area. Furthermore, with industrial use of p.r. hard chromium it is noted that, even though it is possible to deposit crack free coatings, cracks can arise later as a consequence of mechanical or thermal loading.

References

- [1] P. Leisner, D. Ulrich and P. Møller, *Plat. Surf. Finish.* **79**(7) (1992) 62–6.
- [2] W. Clauberg, *Metalloberfläche* **43** (1989) 9.
- [3] C. A. Snavely, *Trans. Electrochem. Soc.* **92** (1947) 537.
- [4] F. A. Lowenheim (ed.), 'Modern Electroplating' (3rd edn), John Wiley & Sons, New York (1974).
- [5] Gmelins 'Handbuch der Anorganischen Chemie', System no. 52, Verlag Chemie, Weinheim (1963).
- [6] W. Eildender, H. Arend and E. Schmidtman, *Metalloberfläche* **2** (1948) 141.
- [7] St. G. Christov and N. A. Pangarov, *Z. Elektrochemie* **61**(1) (1957) 113.
- [8] V. G. Kakovkina and A. N. Sysoev, *Trudy Kharkovsk. Politekh. Inst., Ser. Khim.-Teckhnol.* **18**(5) (1958) 107; *Chem. Abstr.* **54** (1960) 24001.
- [9] C. Colombini, EBRATS 89, São Paulo, Brazil, October (1989).